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(54) MOISTURE-CROSSLINKABLE POLYURETHANE RESIN COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain the subject composition capable of giving touch molded products causing no whitening phenomenon and with good appearance, and free from defects such as pinholes, and useful as a slash molding material, by using a specific surface-modified polyurethane resin powder and a heat-latent catalyst.

SOLUTION: This composition comprises (A) surface-modified polyurethane resin power prepared by treating (i) the particle surface of a powdery thermoplastic polyurethane resin with (ii) a hydrolyzable silane compound and (B) a heat-latent catalyst manifesting such catalytic action as to promote the hydrolysis of the silyl group in the component (ii) at a given temperature, wherein it is preferable that the component (i) is a thermoplastic polyurethane resin having at least one OH group and/or amino group in one molecule, the component B is e.g. a compound formed by neutralizing a protonic acid or Lewis acid with a Lewis base, and the content of the component B is 0.01-10 wt.% based on the total weight of the component A and B.

JAPANESE

[JP,11-228833,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS EXAMPLE

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to a humidity cross-linking polyurethane resin composition. Especially in more detail, when it uses as a charge of slush molding material, it is related with the humidity cross-linking polyurethane resin composition which gives the shaping sheet which has outstanding appearance, solvent resistance, lightfastness, smooth nature, resin strength, etc.

[0002]

[Description of the Prior Art]Since a slush molding method has advantages, like that the product of complicated shape (undercut ** deep drawing etc.) can fabricate easily, that thickness is made uniformly, and the rate of the yield of material is good, it is widely used for the use centering on the interior material of a car, etc. in recent years.

Elastic polyvinyl chloride (henceforth PVC) powder is mainly used for such a use.

However, since elasticity-ized PVC contains a low-molecular plasticizer so much, In prolonged use, the oil film was formed in the windshield of vehicles, etc. by volatilization of a plasticizer (fogging), the driver's visibility was checked and there were disappearance of the lusterless effect by shift of the plasticizer on the surface of a molded product or a soft feeling and a problem of yellowing according to temporal degradation of PVC further. The trial which makes the thing of

desired physical properties profitably like as what improves such a problem using polyurethane resin is performed (for example, JP,2-38453,A, JP,3-97712,A). The polyurethane powder in which especially the interior material of a car back-constructs a bridge by a blocked isocyanate in urethane resin as what solvent resistance and lightfastness are demanded and fills these military requirements is proposed (for example, JP,5-230163,A).

[0003]

[Problem(s) to be Solved by the Invention] However, by what constructs a bridge by a blocked isocyanate, urethane resin. Since the rise of the resin viscosity by bridge construction took place simultaneously with melting of resin at the time of shaping, air bubbles bit in resin and there was a problem that a pinhole occurred in the strength reduction, the appearance defect (white blush mark), undercut part, and edge part of a shaping sheet.

[0004]

[Means for Solving the Problem] This invention persons reached this invention, as a result of inquiring wholeheartedly that said technical problem should be solved. Namely, a forming process after this invention's carrying out hot forming of resin composition for slush molding; characterized by comprising the following, and the above-mentioned resin composition, wherein it carries out humidity bridge construction of this molded product.

A surface denaturation polyurethane resin granular material (A) which comes to process a particle surface of powdered thermoplastic polyurethane (A1) with a hydrolytic silane compound (A2). A humidity cross-linking polyurethane resin composition consisting of a heat latent catalyst (B) which reveals a catalysis which promotes a hydrolysis reaction of a silyl group in ** (A2) at constant temperature; this resin composition.

They are other additive agents by plasticizer (C), paints (D), and necessity.

[0005]

[Embodiment of the Invention] The powdered thermoplastic polyurethane (A1) used in this invention is formed from the active hydrogen ingredient (a) and polyisocyanate (b) which consist of low molecule active hydrogen containing compounds (a2) by polymer polyol (a1) and necessity.

[0006] As the above-mentioned polymer polyol (a1), polyether polyol, polyester polyol, polyether ester polyol, polycarbonate polyol, polymeric polyol, and two or more sorts of these mixtures are mentioned. the number average molecular weight of ** (a1) -- usually -- 500-5,000 -- it is 700-3,000 preferably.

[0007] The compounds of the structure which alkylene oxide added to the compounds (for example, dihydric alcohol and dihydric phenol etc.) which have two active hydrogen atoms as polyether polyol, and two or more sorts of those mixtures are mentioned.

[0008] As the above-mentioned dihydric alcohol, ethylene glycol, a diethylene glycol, Propylene glycol, 1, and 3- and 1,4-butanediol, 1,6-hexanediol, Alkylene glycol, such as neopentyl glycol; the dihydric alcohol (for example, thing:1,4-bis(hydroxymethyl)cyclohexane, m-, or p-xylylene glycol given in a JP,45-1474,B specification etc.) etc. which have an annular group are mentioned. As dihydric phenol, bisphenols, such as monocycle polyhydric phenol; bisphenol A, such as pyrogallol, hydroquinone, and phloroglucine, the bisphenol S, and the bisphenol F, are mentioned. Things desirable [among these] are dihydric alcohol.

[0009] As the above-mentioned alkylene oxide, ethyleneoxide (the following EO and brief sketch), Propylene oxide (the following PO and brief sketch), 1,2-, 1,3-, 1,4- or 2,3-butylene oxide, styrene

oxide, and two or more sorts of these concomitant use (a block or random addition) are mentioned. A thing desirable [among these] is concomitant use of a PO independent, and EO and PO.

[0010]As polyester polyol, For example, condensation polyester polyol by one or more sorts of one or more sorts and polycarboxylic acid of the ** aforementioned dihydric alcohol, or its ester plasticity derivative of condensation polymerizations; Polylactone polyol; by the ring opening polymerization of the lactone which uses the ** aforementioned dihydric alcohol as an initiator. And two or more sorts of these mixtures are mentioned.

[0011]as the example of the polycarboxylic acid of the above-mentioned ** -- aliphatic dicarboxylic acid (succinic acid.) Adipic acid, sebacic acid, glutaric acid, azelaic acid, maleic acid, The ester plasticity derivatives (the carbon number of an acid anhydride and an alkyl group is lower alkyl ester of 1-4, etc.) of aromatic dicarboxylic acid (terephthalic acid, isophthalic acid, etc.), such as fumaric acid, and these dicarboxylic acid and two or more sorts of these concomitant use are mentioned.

[0012]As lactone of the above-mentioned **, gamma-butyrolactone, gamma-valerolactone, epsilon-caprolactones, and two or more sorts of these concomitant use are mentioned.

[0013]What is produced by carrying out the esterification reaction of the one or more sorts of the polycarboxylic acid illustrated as a raw material of one or more sorts and said polyester polyol of said polyether polyol, or its ester plasticity derivative as polyether ester polyol, for example, What is produced by making carry out ring opening addition of the one or more sorts of lactone to one or more sorts of said polyether polyol is mentioned.

[0014]As polycarbonate polyol, polyhexamethylene carbonate diol, polytetramethylene carbonate diol, and two or more sorts of these concomitant use are mentioned, for example.

[0015]The polyol (for example, 5 to 30 % of the weight of polymer contents) which polymerizes and makes-izing [vinyl monomers (for example, styrene, acrylonitrile, etc.)] under existence of a radical polymerization initiator in above mentioned polymer polyol come [dispersion stability] as polymeric polyol is mentioned.

[0016]Desirable things are polyether polyol, polyester polyol, and polycarbonate polyol among the above-mentioned polymer polyol (a1).

[0017]As low molecule active hydrogen containing compounds (a2), the monoamine (a2-3) and monohydric alcohol (a2-4) as low molecule polyol (a2-1), polyamine or these ketimine compounds (a2-2), and a terminator are mentioned.

[0018]The dihydric alcohol illustrated, for example as a starting material of all said polyether RUPORI as low molecule polyol (a2-1). These alkylene oxide low mol additions (less than 500 molecular weight), the alkylene oxide low mol additions (bisphenol A, the bisphenol S, the bisphenol F, etc.) (less than 500 molecular weight) of bisphenols, and two or more sorts of these concomitant use are mentioned.

[0019]As polyamine or these ketimine compounds (a2-2), amines and these ketimine compounds, such as polyamine and polyamide polyamine, are mentioned.

[0020]As the above-mentioned polyamine, an aromatic diamine [phenylenediamine, toluenediamine, 4,4'-diaminodiphenylmethane, m-, or p-xylylene diamine,], such as diethyltoluenediamine, 2,4-, or 2,6-dimethylthiotoluenediamine; Alicyclic diamine [isophoronediamine, 4,4'-diaminoheptylmethane, 4,4'-diamino-3,3'-dimethyldi cyclohexylmethane,], such as 4,4'-diamino-3,3'-dimethyldi cyclohexyl and diaminocyclohexane;

Aliphatic diamine [ethylenediamine,]; alkanolamine derivative, such as 1,6-hexamethylenediamine [N-(2-aminoethyl) ethanolamine] etc.; hydrazine or its derivative [adipic acid dihydrazide] etc., and two or more sorts of these mixtures are mentioned.

[0021]As polyamide polyamine, the condensation reaction thing of dimer acid (polymerized fatty acid) and ethylenediamine of the superfluous equivalent, etc. are mentioned, for example.

[0022]As a ketimine compound, the reactants (acetone, methyl ethyl ketone, methyl isobutyl ketone, etc.) of the above-mentioned polyamine and ketone are mentioned.

[0023]Things desirable [among these] are a ketimine (ASECHIMIN) ghost with acetone of aliphatic diamine, and an ASECHIMIN ghost of alicyclic diamine.

[0024]As monoamine (a2-3) used as occasion demands as a terminator, Alkylamine (ethylamine, a butylamine, diethylamine, di-n-butylamine, etc.) of the carbon numbers 1-8 of an alkyl group, alkanolamines (monoethanolamine, dipropanolamine, diethanolamine, etc.), etc. are mentioned.

[0025]As univalent alcohol (a2-4), methanol, ethanol, n-butanol, cellosolve; the alkylene oxide adducts (phenol, cresol, etc.) (less than 400 molecular weight) of the alkylene oxide adduct (less than 300 molecular weight); univalent phenols of these, etc. are mentioned.

[0026]As polyisocyanate (b), aliphatic series polyisocyanate [ethylene di-isocyanate of the carbon numbers (except for carbon in an NCO group) 2-12, Tetramethylene di-isocyanate, hexamethylene di-isocyanate, Dodeca methylene di-isocyanate, 2,2,4-trimethylhexane diisocyanate,], such as lysine diisocyanate and 2,6-diisocyanatomethyl caproate; Alicyclic poly ISOSHI art [isophorone diisocyanate of the carbon numbers (except for carbon in an NCO group) 4-15, 4 and 4'-dicyclohexylmethane diisocyanate, cyclohexylene diisocyanate,], such as methyl cyclohexylene diisocyanate; Aroma aliphatic series diisocyanate [xylylene diisocyanate of the carbon numbers (except for carbon in an NCO group) 8-12,], such as alpha, alpha, alpha', and alpha'-tetramethyl xylylene diisocyanate; Aromatic diisocyanate [tolylene diisocyanate,], such as diethylbenzene diisocyanate, diphenylmethane diisocyanate, and naphthylene diisocyanate, -- the denaturation thing (a carbodiimide group, an urethodione group, and an isocyanurate group.) of diisocyanate of these Denaturation thing; containing a uret group etc. and two or more sorts of these concomitant use are mentioned.

[0027]Among what was illustrated as these (b), a desirable thing, It is aliphatic series diisocyanate and cycloaliphatic diisocyanate, and especially desirable things are hexamethylene di-isocyanate (the following HDI and brief sketch), isophorone diisocyanate (the following IPDI and brief sketch), and dicyclohexylmethane diisocyanate.

[0028]As a manufacturing method of powdered thermoplastic polyurethane (A1), although the method of the following ** - ** can be illustrated, it is not limited to these, for example.

** Under a non-solvent or existence (toluene, xylene, ethyl acetate, butyl acetate, acetone, methyl ethyl ketone, etc.) of a solvent, To polyisocyanate (b), by polymer polyol (a1) and necessity, low molecule polyol (a2-1), How to carry out freezing pulverization of the polyurethane resin produced by NCO/OH equivalent ratio usually distilling off a solvent as occasion demands after carrying out a polymerization reaction to a package by 0.85-0.95 preferably, 0.8 to 0.98, and.

** Under a non-solvent or existence of a solvent, make (a2-1) react to superfluous (b) by (a1) and necessity, and it is considered as an isocyanate group end urethane prepolymer (b1), How to carry out freezing pulverization of the polyurethane resin produced by distilling off a solvent as occasion demands after making a terminator (a2-3) and/or (a2-4) react to ** (b1) by a chain extension agent

(a2-2), and/or (a2-1) and necessity.

** The urethane prepolymer (b1) obtained under a non-solvent or existence of a solvent is distributed to underwater [containing dispersion stabilizer], How to add (a2-3)/or (a2-4) to this dispersing element by (a2-2) and/or (a2-1), and necessity, carry out a chain elongation reaction to it, consider it as the aqueous dispersion of polyurethane resin, and dry this.

** the nonaqueous system carrier fluid (hexane.) which contains dispersion stabilizer for the urethane prepolymer (b1) obtained under a non-solvent or existence of a solvent How to distribute in heptane etc., to add (a2-3) and/or (a2-4) to this nonaqueous dispersing element by (a2-2) and/or (a2-1), and necessity, carry out a chain elongation reaction to it, consider it as the nonaqueous dispersing element of polyurethane resin, and dry this.

Among described methods, molecular weight control is easy, there is also little amount of the solvent used and especially the method of ** is preferred from the point that moreover (A1) of desired particle diameter is obtained directly.

[0029]As for the mean particle diameter of ** (A1), it is preferred that it is 10-500 micrometers, and it is still more preferred that it is 50-300 micrometers.

[0030]As for ** (A1), it is desirable to usually have preferably a hydroxyl group and/or one or more amino groups 2-4 pieces or more in the molecular terminal and/or molecular side chain. Although the method in particular of introducing a hydroxyl group and/or an amino group into the molecule of ** (A1) is not limited, the following method can be illustrated, for example.

(1) the method of the above-mentioned ** -- a hydroxyl group -- a molecular terminal -- having (A1) -- it is obtained.

(2) using an alkanolamine derivative [for example, N-(2-aminoethyl) ethanolamine or its ketimine compound] as (a2-2) by the method of the above-mentioned ** - ** -- a hydroxyl group -- a molecular side chain -- having (A1) -- it is obtained.

(3) using alkanolamines (for example, monoethanolamine, diopropanolamine, diethanolamine, etc.) as (a2-3) by the method of the above-mentioned ** - ** -- a hydroxyl group -- a molecular terminal -- having (A1) -- it is obtained.

(4) using the above-mentioned alkanolamine as (a2-3) by the method of the above-mentioned ** - **, using the above-mentioned alkanolamine derivative as (a2-2) -- a hydroxyl group -- a molecular side chain and a molecular terminal -- having (A1) -- it is obtained.

(5) using (a2-2) of the superfluous equivalent to the isocyanate group of an isocyanate group end urethane prepolymer (b1) by the method of the above-mentioned ** - ** -- a molecular terminal -- an amino group -- having (A1) -- it is obtained.

[0031]When performing a urethane-ized reaction in the method of the aforementioned ** - **, the catalyst usually used for polyurethane as occasion demands can be used. As an example of this catalyst,] and two or more sorts of these concomitant use, such as organic metallic compound [dibutyltin dilaurate, dioctyltin laurate], etc.; amines [triethylamine, triethylenediamine, and diazabicycloundecen, are mentioned, for example. Although the amount of the catalyst used does not have limitation in particular, it is 0.001 to usual 0.05 weight section per polyurethane resin or isocyanate group end urethane prepolymer (b1) 100 weight section.

[0032]Although the dispersion stabilizer in particular used in the manufacturing method of the above-mentioned ** or ** is not limited, For example, polyvinyl alcohol; Polyoxyethylene chain content polyurethane, For example, polyneopentyl adipate diol. the number average molecular

weight 2. PO and EO of 000/IPDI / polyethylene glycol. (The rate of PO and EO is 20/80 at a weight ratio) A coaddition product. (Number average molecular weight 2,000) [1/1/1 mol] reactant; -- sodium salt [of carboxyl group content vinyl polymer (for example, [styrene / methyl methacrylate / maleic anhydride copolymer] (copolymerization mole ratio 35/15/50))]; -- a cellulose. For example, methyl cellulose; a polyethylene glycol etc. are mentioned.

[0033]Although the dispersion machine in particular used in the method of the above-mentioned ** or ** is not limited, a low-speed shear type dispersion machine, a high-speed shear type dispersion machine, a rubbed type dispersion machine, a high pressure jet type dispersion machine, an ultrasonic wave type dispersion machine, a stood [still] type dispersion machine, etc. are mentioned, for example. Things desirable [among these] are high-speed shear type dispersion machines (for example, the "ultra De Dis parser" by Yamato Scientific and "EBARAMAIRUDA" (by Ebara etc.) etc.), and stood [still] type dispersion machines, such as for example, a "static mixer" (by Tacmina etc.).

[0034]the equivalent ratio [NCO/OH] of the NCO group at the time of manufacturing an isocyanate (NCO) group end urethane prepolymer (b1) in the method of the aforementioned ** - **, and an OH radical -- usually -- 1.01-2.8 -- it is 1.3-2.5 preferably. The NCO content in ** (b1) is usually 2 to 10 % of the weight preferably one to 20% of the weight. If a NCO content exceeds 20 % of the weight, it may become the tendency for the pliability of the molded product obtained from a heat cross-linking polyurethane resin composition to fall, and it may become the viscosity obtained (b1) becomes high too much, and difficult to distribute less than 1% of the weight of a case to underwater or the inside of nonaqueous system carrier fluid.

[0035]In the method of the aforementioned ** - **, (a2-2) as a chain extension agent and/or 0.5-1.5 Eq of the amount of (a2/1 used) are usually 0.7-1.2 Eq preferably to 1 Eq of NCO groups in a prepolymer (b1). Out of this range, resin strength may become insufficient.

[0036]0.5 Eq or less of the amount of (a2-3) as a terminator and/or (a2-4 used) is usually 0.3 Eq or less preferably to 1 Eq of inner (b1) NCO groups. If 0.5 Eq is exceeded, resin strength may fall.

[0037]the number average molecular weight of the powdered thermoplastic polyurethane (A1) used by this invention -- usually -- 5,000-80,000 -- it is 10,000-50,000 preferably. By less than 5,000, good resin strength may not be obtained, if 80,000 is exceeded, the thermal fusibility of a constituent may not become sharp, but the surface smoothness of a molded product may become insufficient. the molecular weight per a hydroxyl group or amino group -- usually -- 500-10,000 -- desirable -- 800-8,000 -- it is 1,000-5,000 especially preferably. By less than 500, it becomes the tendency for the pliability of a molded product to fall, and when 10,000 is exceeded, the lightfastness and solvent resistance of a molded product may become insufficient.

[0038]The content of the sum total of a urethane group (-NHCOO-) and an urea group (-NHCONH-) based on the isocyanate group in ** (A1) is usually 5 to 15 % of the weight preferably three to 20% of the weight. Resin strength sufficient at less than 3 % of the weight may not be obtained, and if 20 % of the weight is exceeded, it will become the tendency for the pliability of resin after bridge construction to fall.

[0039]As a hydrolytic silane compound (A2) used in this invention, it is a following general formula (1).

(X) m-Si-(OR)_{4-m} (1)

The hydrocarbon group of the carbon numbers 1-12 or vinyl group which may have a basis as

which X are chosen from an acryloxy (meta) group, an epoxy group, a glycidoxyl group, an amino group, a sulphydryl group, and an isocyanate group among [type, and R are the alkyl group or methoxy alkyl group of the carbon numbers 1-4. [However, (OR) of an individual (4-m) may be the same, or may differ. Expressing J, m is 0, 1, or 2. The compound shown by] is mentioned. As an example of this compound, for example A non-functionality Silang [tetramethoxy silane, A tetraethoxysilane, methyl trimethoxysilane, methyl triethoxysilane,], such as dimethyl diethoxysilane, isobutyl trimethoxysilane, decyltrimetoxysilane, phenyltrimethoxysilane, diphenyldimethoxysilane, phenyltriethoxysilane, and diphenyl diethoxysilane; unsaturation group functionality Silang [vinylsilane [Vinyltrimetoxysilane, vinyltriethoxysilane, vinyltris (beta-methoxyethoxy) Silang], etc. Acryloxy (meta) silane [gamma-(meta) acryloxypropyltrimethoxysilane, gamma-(meta) acryloxypropyltriethoxysilane, gamma-(meta) acryloxypropylmethyldimethoxysilane, gamma-(meta) acryloxypropylmethyldiethoxysilane], etc. **]; Epoxy functionality Silang [gamma-glycidoxypropyltrimetoxysilane,]; amine functionality Silang [N-beta-(aminoethyl)-gamma-aminopropyl trimethoxysilane, such as gamma-glycidoxypropylmethyldiethoxysilane and beta-(3,4-epoxycyclohexyl) ethyltrimethoxysilane, N-beta-(aminoethyl)-gamma-aminopropyl methyl dimethoxysilane,], such as gamma-aminopropyl triethoxysilane and N-phenyl-gamma-aminopropyl trimethoxysilane; Mercapto functionality Silang [gamma-mercapto propyltrimethoxysilane,], such as gamma-mercaptopropylmethyl dimethoxysilane; Isocyanate functionality Silang [gamma-isocyanato propyltrimethoxysilane,]; and these two or more sorts of mixtures, such as gamma-isocyanatopropyl triethoxysilane, gamma-isocyanato propylmethyl dimethoxysilane, and gamma-isocyanate propylmethyl diethoxysilane, are mentioned. Things desirable [among these] are non-functionality Silang, epoxy functionality Silang, and isocyanate functionality Silang, Especially desirable things are diphenyldimethoxysilane, diphenyl diethoxysilane, gamma-glycidoxypropyltrimetoxysilane, gamma-isocyanato propyltrimethoxysilane, and gamma-isocyanatopropyl triethoxysilane.

[0040]The content of this hydrolytic silane compound (A2) in surface denaturation POURETAN resin powder (A) is usually 0.5 to 5 % of the weight preferably 0.1 to 10% of the weight to the weight of powdered thermoplastic polyurethane (A1).

[0041]Although the method in particular of processing the particle surface (or the neighborhood) of ** (A1) by ** (A2) is not limited, the following method can be illustrated, for example.

** (A2) How to remove an organic solvent after mixing (A1) with the organic solvents (for example, hexane, heptane, ethyl acetate, toluene, xylene, etc.) made to contain.

** a granular material blender etc. -- using (A1) -- how to remove an organic solvent after carrying out the spray of the organic solvent solution while stirring (A2) and mixing.

The method of ** is preferred from an industrial standpoint among described methods.

[0042]The heat latent catalyst (B) used by this invention is constant temperature (70 ** usually). By heating preferably more than 100 **, an acid catalyst or a basic catalyst is reproduced and it acts as a catalyst which promotes the hydrolysis reaction (crosslinking reaction) by the humidity of the hydrolytic silyl group which exists in (A). As ** (B), the compound which neutralized proton acid by the Lewis base, the compound which neutralized Lewis acid by the Lewis base, sulfonic ester, phosphoric ester, amine imide compounds, various onium compounds, and two or more sorts of these mixtures are mentioned, for example.

[0043]As a compound which neutralized the above-mentioned proton acid by the Lewis base, For

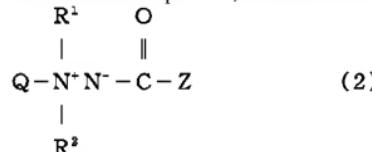
example, halogeno carboxylic acid and sulfonic acid (for example, monochloroacetic acid etc.) (for example, the following), Sulfuric acid monoalkyl (carbon numbers 1-12) ester species and phosphoric acid mono- ***** Dialkyl (carbon numbers 1-12) ester species (for example, the following), Boric acid mono- ***** proton acid, such as dialkyl (carbon numbers 1-12) ester species, amines (ammonia, triethylamine, pyridine, aniline, piperidine, morpholine, monoethanolamine, etc.), trialkylphosphine, and doria -- the compound neutralized by Lewis bases, such as real phosphine and trialkyl (carbon numbers 1-8) phosphite, is mentioned.

[0044]As a compound which neutralized Lewis acid by the Lewis base, the compound etc. which neutralized Lewis acid, such as BF_3 , FeCl_3 , SnCl_3 , AlCl_3 , and ZnCl_2 , by the aforementioned Lewis base are mentioned, for example.

[0045]As the above-mentioned sulfonic ester, for example Sulfonic acid, such as methanesulfonic acid, benzenesulfonic acid, alkyl (carbon numbers 1-12) benzenesulfonic acid, and naphthalene sulfonic acid. The esterification material of secondary alcohol, such as the primary alcohol, such as ethanol, n-propanol, n-butanol, and 2-ethylhexanol, or isopropanol, and 2-butanol, etc. are mentioned.

[0046]As the above-mentioned phosphoric ester, the phosphoric acid mono- ***** diester of secondary alcohol, such as the primary alcohol, such as ethanol, n-propanol, n-butanol, and 2-ethylhexanol, or isopropanol, and 2-butanol, is mentioned, for example.

[0047]As amine imide compounds, it is a following general formula (2), for example.



The alkyl group or aralkyl group of the carbon numbers 1-10 in which Q may have a hydroxyl group among [type, The alkyl group of the carbon numbers 1-10 from which R¹ and R² are the same as or different, and Z express the fatty acid residue or oxy acid residue which has the straight chain or branched chain of the saturation of the carbon numbers 2-24, or an unsaturation. The compound shown by] is mentioned and 1,1,1, - trimethylamine butylimide, 1,1-dimethyl- 1-(2-hydroxypropyl) amine ethylimide, 1,1-dibutyl- 1-(2-hydroxypropyl) amine octylimide, etc. are mentioned as an example.

[0048]As an onium compound, it is following general formula (3) - (7), for example.

$[\text{R}^1_3\text{NR}^3]^+$ and X^- (3)

$[\text{R}^1_3\text{PR}^3]^+$ and X^- (4)

$[\text{R}^1\text{R}^2\text{OR}^3]^+$ and X^- (5)

$[\text{R}^1\text{R}^2\text{SR}^3]^+$ and X^- (6)

$\text{X}^- \cdot [\text{R}^1\text{R}^2\text{S-}\text{phSph-SR}^3\text{R}^4]^{2+}$ and X^- (7)

Independently R¹ and R² among [type, respectively The alkyl group of the carbon numbers 1-12, An alkenyl group, an aryl group, an alkyl aryl group, or a cycloalkyl group. (however, two R¹ or R¹, and R² may form the heterocycle which combines with each other and uses N, P, O, or S as a

hetero atom.). Independently R³ and R⁴, respectively The alkyl group of the carbon numbers 1-12, As for an alkenyl group, an aryl group, an alkyl aryl group or a hydrogen atom, and ph, a phenylene group and X⁻ express SbF₆⁻, AsF₆⁻, PF₆⁻, or BF₄⁻. The ammonium compound, the phosphonium compound, oxonium compound, and sulfonium compound which are shown by] are mentioned. As an ammonium compound, tetramethylammonium and a SbF₆ salt, trimethylbenzylammonium and a PF₆ salt, methyl triethyl ammonium and a BF₄ salt, methylethyl mol HORINIUMU, a SbF₆ salt, etc. are mentioned, for example. As a phosphonium compound, methyl tributyl phosphonium and a SbF₆ salt, methyltriphenylphosphonium and an AsF₆ salt, FENIRUTORI cresyl phosphonium and an AsF₆ salt, tetraphenyl phosphonium, a BF₄ salt, etc. are mentioned, for example. As an oxonium compound, triethyloxonium and a BF₄ salt, methyldiphenyloxonium, a PF₆ salt, etc. are mentioned, for example. As a sulfonium compound, for example Butyldiphenyl sulfonium and a PF₆ salt, Triphenylsulfonium and a SbF₆ salt, phenylthiophenyl diphenyl sulfonium and a SbF₆ salt, a 4,4'-bis(diphenyl sulfonium) diphenylthioether, a PF₆ salt, etc. are mentioned.

[0049]The catalyst (B) illustrated above can be used combining one sort or two sorts or more. The inside of the sulfonium compound in which a thing desirable [among these] is shown by the above-mentioned general formula (6) and (7), Are SbF₆⁻ or PF₆⁻ the aromatic sulfonium salt which it has as an anion kind, and especially a desirable thing, They are a PF₆ salt of the 4,4'-bis(diphenyl sulfonium)diphenylthioether of the disulfo NIUMU compounds shown by a general formula (7), and a SbF₆ salt.

[0050]The quantity of ** (B) is usually 0.05 to 5 % of the weight preferably 0.01 to 10% of the weight based on the total weight of (A) and (B). Sufficient catalysis is revealed without degrading a molded product by carrying out within the limits of this.

[0051]As a method of making (B) containing in the humidity cross-linking polyurethane resin composition of this invention, the following method can be illustrated, for example.

** How to add the catalyst (B) beforehand in the arbitrary stages in manufacture of said powdered polyurethane resin (A1).

** How to carry out the spray of the organic solvent solution of (B), and mix while stirring said surface treatment polyurethane resin granular material (A) with a granular material blender etc.

** How to make (B) contain in the organic solvent solution of ** (A2) when processing the particle surface of the above (A1) by (A2).

The method of ** and ** is preferred among described methods.

[0052]10-500 micrometers of mean particle diameter of the humidity cross-linking polyurethane resin composition of this invention are usually 50-300 micrometers preferably. In less than 10 micrometers, a granular material is charged or it is easy to generate dust, and the melting nature of the grain child over 500 micrometers worsens, and mean particle diameter serves as the tendency for the appearance of a molded product to be spoiled. mean particle diameter here -- for example, the particle-size-distribution instrumentation system for processes -- it can measure using "TSUB-

TEC300 [the Nippon Mining Co., Ltd. make]."

[0053]The granular material of the humidity cross-linking polyurethane resin composition of this invention and the powder-mixing thing which serves as a plasticizer (C) and paints (D) from other additive agents (an antiblocking agent, a release agent, etc.) as occasion demands are suitably used as a charge of slash molding material.

[0054]As the above-mentioned plasticizer (C), phthalic ester [dibutyl phthalate,], such as dioctyl phthalate, phthalic acid benzyl butyl ester, and diisodecyl phthalate; Aliphatic series dibasic acid ester [di(2-ethylhexyl) adipate,], such as sebacic acid-2-ethylhexyl; Trimellitic acid ester [tri-trimellitic acid 2-ethylhexyl,], such as trimellitic acid trietyl; phosphoric ester [phosphoric acid tri-2-ethylhexyl, trietyl phosphate, phosphoric acid TORIKUREJIRU], etc.; fatty-acid-ester [butyl oleate] etc.; and two or more sorts of these mixtures are mentioned. Phthalic ester and phosphoric ester are [among these] preferred. The loadings of a plasticizer are usually three to 20 weight section preferably one to 30 weight section to humidity cross-linking polyurethane resin composition 100 weight section.

[0055]Especially as the above-mentioned paints (D), it is not limited but a publicly known organic color and/or inorganic pigment can be used. As an organic color, they are mentioned by insoluble azo pigment, soluble azo pigment, copper-phthalocyanine system paints, quinacridone paints, etc., and as inorganic system paints, Chromate salt, a ferro cyanide compound, a metallic oxide, a sulfide selenium compound, metal salt, metal powder (sulfate, silicate, carbonate, phosphate, etc.), carbon black, etc. are mentioned. The loadings of paints are usually one to 5 weight section preferably 0.5 to 10 weight section to humidity cross-linking polyurethane resin composition 100 weight section.

[0056]Especially as the above-mentioned antiblocking agent, it is not limited but a publicly known inorganic system antiblocking agent or an organic system antiblocking agent can be used. As an inorganic system antiblocking agent, silica, talc, titanium oxide, calcium carbonate, etc. are mentioned, as an organic system antiblocking agent -- thermosetting resin (for example, thermosetting polyurethane resin, guanamine system resin, epoxy system resin, etc.) with a particle diameter of 10 micrometers or less and with a particle diameter of 10 micrometers or less thermoplastics [-- for example,], such as thermoplastic polyurethane and poly (meta) acrylate resin, is mentioned. The loadings of an antiblocking agent are usually 0.05 - the amount part of duplexs to humidity cross-linking polyurethane resin composition 100 weight section.

[0057]A publicly known release agent can be used as the above-mentioned release agent. As this release agent, for example A fluorine system release agent (phosphoric acid fluoro alkyl ester etc.), a silicon system release agent (dimethylpolysiloxane and amino modifying dimethylpolysiloxane.) Fatty-acid-ester system release agents [alkane (carbon numbers 11-24) acid alkenyl (carbon numbers 6-24) ester] etc., such as carboxyl denaturation dimethylpolysiloxane, a phosphoric ester system release agent (tributyl phosphate ester), etc. are mentioned. The loadings of a release agent are usually 0.05 - the amount part of duplexs to humidity cross-linking polyurethane resin composition 100 weight section.

[0058]When blending the above-mentioned additive agent etc. with the granular material of the humidity cross-linking polyurethane resin composition of this invention, a publicly known powder-mixing device can be used. as the example of this powder-mixing device -- high-speed-shearing mixing device [-- the Mitsui Mining Co., Ltd. make -- " passing -- NSHIERU mixer" and the

product made from Fukae Industry -- "--], such as high speed mixer", a low-speed mixing device ["NAUTA mixer" by Hosokawa Micron CORP. etc.], etc. are mentioned. By the above (C), (D), and necessity, other additive agents, Although it is preferred to mix with the granular material of a humidity cross-linking polyurethane resin composition, these parts or all may be beforehand added in the arbitrary stages in the manufacturing stage of powdered thermoplastic polyurethane (A1), or the manufacturing stage of a resin composition.

[0059]As other additive agents, weatherproof stabilizer, lubricant, heat-resistant stabilizer, fire retardant, etc. are mentioned.

[0060]The humidity cross-linking polyurethane resin composition of this invention, Although the molded product (or coat) where crosslinking reaction advanced and which was excellent in lightfastness and solvent resistance by recuperating oneself under humidity existence after melt molding in a granular material is given and the molded product which fully carried out surface crosslinking also of the ordinary temperature normal relative humidity (for example, 25 **, 65% RH) by the care of health for about one week is usually obtained, When bridge construction speed needs to be increased further, it is possible to obtain an object more for a short time by processing the surface of a molded product with steam, hot and cold water, etc., before recuperating oneself under high-humidity/temperature (for example, 60 **, 90%RH) or carrying out post forming cooling.

[0061]The humidity cross-linking polyurethane resin composition of this invention, Since the hardened material excellent in weatherability, solvent resistance, adhesive strength, resin strength, etc. is given, it can be used for the use of various molding material and thermofusion type adhesives (for example, adhesives for adhesion padding cloths, etc.), powder coatings, etc., and can use conveniently as a charge of slush molding material especially.

[0062]A slush molding method is a method of contacting the above-mentioned powder-mixing thing to the heated metallic mold, and making a sheet forming. The die temperature at this time is 200-240 **, and contact time is usually several seconds - a for [1 minute] grade. By having formed the sheet in the metallic mold, and also pouring in the charges of foam (polyurethane foam material etc.), and carrying out adhesion foaming, the final mold goods which use this sheet as an epidermis layer are obtained. These mold goods are used for the various interior materials of a car, interior furniture, etc.

[0063]

[Example]Hereafter, although an example explains this invention further, this invention is not limited to this. Below, each of parts, %, and ratios is weight references. Mean particle diameter was measured using "TSUB-TEC300" by Nippon Mining Co., Ltd.

[0064]90 copies of di-isodecyl phthalate and ten copies of carbon black (HCF grade) were taught to the reaction vessel provided with example 1 rabble, and it mixed until it became uniform. Let the obtained mixture be [the colorant 1].

[0065]The hydroxyl number supplied 2,200 copies of neopentyl horse mackerel peat diol of 56 to the reaction vessel provided with example 1 rabble and the thermometer, it heated at 110 ** under decompression of 3mmHg, and drying was performed for 1 hour. Then, 488 copies of IPDI(s) were supplied and the urethane prepolymer which performs a reaction at 120 ** for 8 hours, and has an isocyanate group at the end was obtained. The NCO content of this prepolymer was 3.4%. To 195.5 copies of this prepolymer, 17.5 copies of diketimine ghosts of IPDA and acetone, After adding 2.1

copies of diethanolamines, and [colorant 1] 24 copy and mixing uniformly at 25 **, 1,200 copies of concentration PVA solutions were added 1%, the URUTORADESU parser (made by Yamato Scientific) was used, and it mixed for 1 minute at the number of rotations of 6,000 rpm. After stirring for further 3 hours and completing a reaction, the line of filtration and the desiccation was carried out and the powder (S1) of the thermoplastic polyurethane resin composition was obtained. To this, stirring 209 copies of ** (S1) by a high speed mixer Diphenyldimethoxysilane ["KBM202" by Shin-Etsu Chemical Co., Ltd.] 9.8 copy, 0.1 copy of dibutyltin dilaurate, and heat latent catalyst [3 Product "SAN-AID SI-150L" made from Japanese Federation of Chemical Industry Workers' Unions Industry] Carry out the spray of the solution which dissolved one copy in ten copies of ethyl acetate / n-heptane (50/50) partially aromatic solvents, and it is added, After mixing uniformly, it dried at 50 ** for 3 hours, and 218 copies of colored powder (P1) of the humidity cross-linking polyurethane resin composition of this invention were obtained. The mean particle diameter of ** (P1) was 165 micrometers.

[0066]In example 2 Example 1, replace with 9.8 copies of diphenyldimethoxysilane and it is made to be the same as that of Example 1 except having used the 3-triethoxy silyl propylisocyanate ["KBE-9007" by Shin-Etsu Chemical Co., Ltd.] 9.9 copy, 219 copies of colored powder (P2) of the humidity cross-linking polyurethane resin composition of this invention were obtained. The mean particle diameter of ** (P2) was 170 micrometers.

[0067]The hydroxyl number supplied 2,200 copies of neopentyl horse mackerel peat diol of 56 to the same reaction vessel as comparative example 1 Example 1, it heated at 110 ** under decompression of 3mmHg, and drying was performed for 1 hour. Then, 488 copies of IPDI(s) were supplied and the urethane prepolymer which performs a reaction at 120 ** for 8 hours, and has an isocyanate group at the end was obtained. The NCO content of this prepolymer was 3.4%. To 195.5 copies of this prepolymer, 17.5 copies of diketimine ghosts of IPDA and acetone, After adding the epsilon caprolactam adduct ["duranate tPA-100" by Asahi Chemical Industry Co., Ltd.] 11.2 copy of 2.1 copies of diethanolamines, and the isocyanurate denaturation thing of HDI, and [colorant 1] 24 copy and mixing uniformly at 25 **, 1,200 copies of concentration PVA solutions were added 1%, the URUTORADESU parser (made by Yamato Scientific) was used, and it mixed for 1 minute at the number of rotations of 6,000 rpm. After stirring for further 3 hours and completing a reaction, filtration and desiccation were performed and 244 copies of colored powder (P3) of the heat cross-linking polyurethane resin composition for comparison were obtained. The mean particle diameter of this resin composition was 220 micrometers.

[0068]It water-cooled and the shaping sheet was created, after having contacted example of system performance testing 1 coloring resin powder (P1) - (P3) to the metallic mold heated at 220 **, respectively for 1 minute, removing the powder of after [thermofusion] non-melting and neglecting it for 1 minute in a room temperature. After neglecting the obtained shaping sheet for one week under 25 ** and the atmosphere of 65% of relative humidity, system performance testing was done with the following test method. The result is shown in Table 1.

White blush mark (appearance); the visual judgment of the sheet surface was carried out.
Pinhole; the shaping sheet was held up to light and the visual judgment of the existence of a pinhole was carried out.

Sheet breaking strength and elongation after fracture (25 **); it measured according to JIS-K6301.
Lightfastness: After carrying out 400 time processings within a carbon arc fadeometer with a black

panel temperature of 83 **, the visual judgment of the appearance on the surface of mold goods was carried out. .

Solvent resistance: 0.1 ml of ethanol was dropped at the shaping sheet with the dropper, and after 25 **x 24-hour maintenance, the surface state was observed for 60 **x 30 minutes for 25 **x 10 minutes, after wiping off a sheet surface with water. The five-step evaluation which made the state where the 5th class and damage were remarkable the 1st class showed changeless *****.

[0069]

[Table 1]

	実施例	実施例	比較例
	1	2	1
樹脂粉末	P 1	P 2	P 3
白化(外観)	無し	無し	有り
ピンホール	無し	無し	有り
シート破断強度(Kg/cm ²)	130	115	40
シート破断伸び(%)	450	400	100
耐光性	変化なし	変化なし	変化なし
耐溶剤性	5級	5級	5級

[0070]

[Effect of the Invention]The humidity cross-linking polyurethane resin composition of this invention has the following effect.

- (1) When it uses as a charge of slush molding material, at the time of shaping, in order not to form the structure of cross linkage, it excels in melting nature, and it does not have albinism, it excels in appearance, and a tough molded product without the defect of a pinhole etc. is obtained.
- (2) After shaping, in order to form the structure of cross linkage in the surface by contacting moisture, the molded product obtained is excellent in lightfastness, solvent resistance, etc.
- (3) Since crosslinking reaction does not advance unless it heats to the elevated temperature of 70 or more **, excel in heat-resistant preservation stability.

Since the above-mentioned effect is done so, especially the humidity cross-linking polyurethane resin composition of this invention is useful as charges of slush molding material, such as an interior material of a car, and useful also as hot melt adhesive and powder coatings, such as adhesives for adhesion padding cloths.

[Translation done.]